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AUTO-DECONTAMINATING SURFACES BASED ON LIGHT-ACTIVATED PHOTOELECTROCHEMICAL DIODE PARTICLES

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This program has dealt with applications of photoelectrochemistry to decontamination. Photoaided decomposition of toxic compounds was demonstrated for solutions and slurries containing noxious substances such as cyanide and organophosphors. Contributions have been made to the electrochemistry of organophosphorous compounds as well as to the understanding of interactions of organophosphorous substances with oxide surfaces.

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SUMMARY

The program started on August 1, 1983 and ended on February 29, 1988. This program is a part of the effort towards finding effective methods of decontamination.

The program was focused on studying the interaction of various solids with warfare chemical agents or simulants thereof. The study was performed on liquid-solid and gas-solid interfaces. The program was divided into three areas of study:

1. Investigation of the electrochemistry of the agents or simulants to determine if they are susceptible to oxidation and reduction reactions.

2. Studies of the photoelectrochemical degradation of the simulants by semiconductors in solution.

3. Evaluation of the gas-solid reactions on surfaces that are potentially active in decontamination.

Our findings can be summarized as follows:

- Particulate oxide semiconductors, appropriately pretreated, can accelerate the decomposition of aqueous cyanide ions under illumination. This fact was demonstrated for platinized titanium dioxide.

- The removal of diisopropyl fluorophosphate is accelerated by illumination of slurries containing n-type semiconductors, such as titanium dioxide or zinc oxide. The illumination must be performed with photons that have energy larger than the bandgap of the oxide (>3 eV).

- Our studies showed that phosphorus-containing organic compounds with the general formula $ROP(O)X_1X_2$ (with $X_{1,2}$ = RO-, Cl-, H-,or H_3C-) are electrochemically stable, even in solvents allowing for large potential windows, such as acetonitrile, and dimethylformamide.

- Zinc oxide and titanium dioxide adsorb dimethyl methylphosphonate (DMMP) in a dissociative form if heated or irradiated with light whose photons have energy larger than the bandgap of the oxide.

- We have shown that the nature of adsorption on DMMP on various oxides correlates very well with thermodynamical properties of the oxides, such as the heat of formation of the metal-oxygen bond of the oxide, or its isoelectric point. The experiments were performed in the series: aluminum oxide, magnesium oxide, titanium oxide, tungsten oxide, and zinc oxide.

Our study indicates that non-catalytic electrochemical treatment of solutions contaminated with organophosphorous compounds is not effective. Our results also indicate that organophosphorous compounds are effectively adsorbed on oxide surfaces. The main body of future work along this path should therefore be directed towards finding better catalysts for decomposition of the adsorbates, as well as for desorption of the products. We made some progress in this direction and our results suggest that catalysis might be favored on the surface of titanium dioxide and tungsten oxide.

Participants:

The following is a list of people that have been involved in the various stages of this project:

Principal Investigator(s)

Dr. Benedict Aurian-Blajeni	-	10/87 to 02/88
Dr. Timothy L. Rose	-	08/83 to 10/87

Senior Scientists

Dr. Benedict Aurian-Blajeni	-	08/87 to 10/87
Dr. Thomas J. Lewis	-	09/85 to 08/87
Dr. Chenniah Nanjundiah	-	08/83 to 09/85

Staff Scientist

Ms. Michele M. Boucher (B.A.)	-	10/87 to 02/88

The conclusions summarized above were presented in various forms and forums. Following is a list of publications and presentations of results sponsored under this contract.

Publications

C. Nanjundiah and T. L. Rose, "Enhancement of the Rate of Photooxidation of CN^- on TiO_2 Photoanodes," Extended Abstract #646, 166th Meeting of The Electrochemical Society, New Orleans, LA, 1984.

T. L. Rose and C. Nanjundiah, "Rate Enhancement of Photooxidation of CN^- with TiO_2 Particles," J. Phys. Chem., 89, 3765 (1985) - Technical Report No. 1.

T. L. Rose and C. Nanjundiah, "Accelerated Decomposition of DFP on Illuminated Semiconductor Particles," Proceedings of the 1985 Scientific Conference on Chemical Defense Research, M. Rausa, Ed., CRDEC-SP-86007, p. 299, 1986 - Technical Report No. 2.

C. Nanjundiah and T. L. Rose, "Cyclic Voltammetric Analysis of Organophosphorous Esters," J. Electrochem. Soc., 133, 955 (1986) - Technical Report No. 3.

C. Nanjundiah and T. L. Rose, "Electrochemical Investigation of Phenylphosphorodichloridate," Extended Abstract #487, 169th Meeting of The Electrochemical Society, Boston, MA, 1986 - Technical Report No. 4.

C. Nanjundiah, T. J. Lewis and T. L. Rose, "Electrochemical Investigation of Phenylphosphorodichloridate," Electrochim. Acta, 33, 279 (1988) - Technical Report No. 5.

T. J. Lewis, B. Aurian-Blajeni and T. L. Rose, "Decomposition Reactions of Dimethyl Methylphosphonate on Heated and Irradiated Semiconductor Surfaces," Proceedings of the 1987 Scientific Conference on Chemical Defense Research, M. Rausa, Ed., to be published in 1988 - Technical Report No. 6.

B. Aurian-Blajeni and M. M. Boucher, "Interaction of Dimethyl Methylphosphonate with Oxides," submitted for publication in Langmuir, Technical Report No. 7.

Public Presentations

Enhancement of the Rate of Photooxidation of CN^- on TiO_2 Photodiodes, by C. Nanjundiah and T. L. Rose, 166th Meeting of The Electrochemical Society, New Orleans, LA, May 1984.

Accelerated Decomposition of DFP on Illuminated Semiconductor Particles, by T. L. Rose and C. Nanjundiah, The 1985 Scientific Conference on Chemical Defense Research, Aberdeen Proving Grounds, MD, November 1986.

Use of Semiconductor Diode Particles for Photodecomposition of Toxic Materials, by T. L. Rose, seminar presented at Haverford College, Haverford, PA, April 1986.

Electrochemical Investigation of Phenylphosphorodichloridate, by C. Nanjundiah and T. L. Rose, 169th Meeting of The Electrochemical Society, Boston, MA, May 1986.

Surface Adsorption and Decomposition of Dimethylmethylphosphonate on ZnO Surfaces, by T. L. Rose and T. J. Lewis, 193rd National Meeting of the American Chemical Society, Denver, CO, April 1987.

Photodecomposition of Dimethylmethylphosphonate on Irradiated ZnO Surfaces, by T. L. Rose, NATO ASI-Double Jump Course on New Trends and Applications of Photocatalysis and Photoelectrochemistry, Cefalu, Sicily, Italy, September 1987.

Decomposition Reactions of Dimethyl Methylphosphonate on Heated and Irradiated Semiconductor Surfaces, by T. J. Lewis, B. Aurian-Blajeni and T. L. Rose, The 1987 Scientific Conference on Chemical Defense Research, Aberdeen Proving Grounds, MD, November 1987.

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